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**WO 02/03143 A2**

(54) Title: **CARBONATE-BASED PHOTORESIST STRIPPING COMPOSITIONS**

(57) Abstract: Compositions useful for removing photoresist from a surface that are less corrosive and do not cause skin irritation. Such compositions comprise an alkylene carbonate, and optionally, either an alcohol, glycol ether, or a dibasic ester. The compositions may also further include water or hydrogen peroxide. Additionally, a method of removing photoresist from a surface. The method involves contacting the surface with an effective amount of a composition that comprises: an alkylene carbonate; optionally, either an alcohol, glycol ether, or a dibasic ester; and, optionally, water or hydrogen peroxide, and allowing the composition to contact the surface for a period of time and under conditions effective to cause the removal of the photoresist from the surface.

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## CARBONATE-BASED PHOTORESIST STRIPPING COMPOSITIONS

## Technical Field

This invention relates to photoresist stripping compositions, and, more particularly, to carbonate-based photoresist stripping compositions and methods of use thereof.

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## Background of the Invention

Photolithography is a process that is used in manufacturing integrated circuits, whereby the pattern of the integrated circuit is imprinted on a wafer, a thin slice of a semiconductor material. The pattern is imprinted on the wafer by first coating the wafer with a photoresist, placing a mask that contains the desired pattern over the coated wafer, and then exposing the wafer to light. If a positive resist is being used, the portion of the exposed resist (i.e. the portion not covered by the mask) will react with the light, and become more soluble in the photoresist remover. After sufficient light exposure, the wafer is then washed with a photoresist remover, which removes the portion of the photoresist that corresponds to the pattern on the mask. Alternatively, if a negative resist is used, the exposed portion of the resist will react with the light to become polymerized, and, hence, insoluble in the photoresist remover. After sufficient light exposure, the wafer is then washed with a photoresist remover, which removes the portion of the photoresist that corresponds to the inverse pattern on the mask.

Numerous photoresist remover compositions have been developed. U.S. Pat. No. 5,690,747 discloses a solvent for removing photoresist that comprises at least one aprotic, alicyclic carbonate and at least one aprotic, polar compound that is used in conjunction with ultrasonic agitation. U.S. Pat. No. 4,438,192 discloses a photoresist stripper that comprises methylene chloride, methanol, and methyl formate. U.S. Pat. No. 4,806,458 discloses a photoresist stripping composition that consist essentially of a hexa-alkyl disilazane and a solvent composition that comprises one or more compounds selected from the group consisting of a propylene glycol monoalkyl ether and a propylene glycol mono-alkyl ether acetate. U.S. Pat. No. 4,824,763 discloses a photoresist removal composition that comprises a triamine and a nonpolar aliphatic or aromatic hydrocarbon or chlorinated hydrocarbon or polar pyrrolidone, dimethyl formamide, or butyrolactone organic solvent. U.S. Pat. No. 4,483,917 discloses a composition for removing an organic positive photoresist composition that comprises N-amino-alkylpiperazine, and/or N-hydroxyalkyl-piperazine, and a pyrrolidone.

Unfortunately, many conventional photoresist stripper compositions contain components that are corrosive or skin irritants. Therefore, a need exists for effective photoresist stripper compositions that are less corrosive and do not cause skin irritation.

### Summary of the Invention

Accordingly, the present invention is directed toward effective photoresist stripping compositions that are less corrosive and do not cause skin irritation.

5 In one embodiment, the present invention provides for compositions useful for removing photoresist from a surface. Such compositions comprise an alkylene carbonate, and optionally, either an alcohol, glycol ether, or a dibasic ester. The compositions may also further comprise water or hydrogen peroxide.

10 In another embodiment, the present invention provides for a method of removing photoresist from a surface. The method involves contacting the surface with an effective amount of a composition that comprises: an alkylene carbonate; optionally, either an alcohol, glycol ether, or a dibasic ester; and, optionally, water or hydrogen peroxide, and allowing the composition to contact the surface for a period of time and under conditions effective to cause the removal of the photoresist from the surface.

### Detailed Description of the Preferred Embodiment

15 In one embodiment, the present invention provides for compositions useful as photoresist removers. These compositions comprise an alkylene carbonate, and optionally, either an alcohol, glycol ether, or a dibasic ester. The compositions may also further comprise water or hydrogen peroxide. Surprisingly, the compositions of the present invention are as effective as conventional photoresist strippers that tend to be more corrosive and irritate the skin, such as those based on 2-(2-aminoethoxy)ethanol. In addition, because  
20 the compositions of the present invention are alkylene carbonate-based, solvent loss is minimal during use because of the high boiling point associated with alkylene carbonates.

Generally, the compositions of the present invention comprise at least about 5% by weight of an alkylene carbonate, from about 0% to about 60% by weight of either an alcohol,  
25 a dibasic ester, or a glycol ether. Optionally, the compositions may also comprise up to about 80% by weight of water, or hydrogen peroxide, or mixtures thereof. Preferably, the compositions of the present invention comprise at least about 30% by weight of an alkylene carbonate, and more preferably, at least about 40% by weight of an alkylene carbonate.

Additionally, the compositions of the present invention may also be based on  
30 compositions comprising JEFFSTRIP™ FST (commercially available from the Huntsman Corporation, Houston, Texas), an alkylene carbonate/hydrogen peroxide-based composition. Representative, although not exhaustive, JEFFSTRIP™ FST compositions are disclosed in U.S. Pat. No. 6,040,284, which is incorporated by reference. Generally, if JEFFSTRIP™ FST is used, the compositions comprise at least about 35% by weight of JEFFSTRIP™ FST,  
35 at least about 25% by weight of either an alcohol, a dibasic ester, or a glycol ether, and,

optionally, at least about 5% by weight of an alkylene carbonate. Preferably, if JEFFSTRIP<sup>TM</sup> FST is used, the compositions comprise at least about 40% by weight of JEFFSTRIP<sup>TM</sup> FST, and at least about 30% by weight of either an alcohol, a dibasic ester, or a glycol ether.

5       The alkylene carbonate used in the present invention may comprise any number of alkylene carbonates or mixtures thereof. Suitable alkylene carbonates have from about two to about eight carbon atoms. Preferably, the alkylene carbonate comprises propylene carbonate, butylene carbonate, or mixtures thereof. More preferably, the alkylene carbonate comprises propylene carbonate.

10       The alcohol used in the present invention may comprise any number of alcohols. Preferably, the alcohol comprises benzyl alcohol, isopropyl alcohol, methanol, or ethanol.

      The glycol ether used in the present invention may comprise any number of glycol ethers. Preferably, the glycol ether comprises diethylene glycol butyl ether or propylene glycol methyl ether.

15       The dibasic ester used in the present invention may comprise any number of dibasic esters, including, but not limited to distilled dimethyl esters of adipic, glutaric, and succinic acids.

      The hydrogen peroxide used in the present invention may be obtained from a variety of commercial sources as an aqueous hydrogen peroxide solution. Such solutions are  
20 commonly available with concentrations ranging from about one to about eighty percent.

      The photoresist removal compositions of the present invention may be used to remove positive or negative photoresist from a variety of surfaces. Preferably, the photoresist removal compositions of the present invention are used to remove negative photoresist from a surface. Such surfaces may include, but are not limited to, aluminum, copper, silicon, or  
25 derivatives thereof.

      In another embodiment, the present invention provides for a method of removing photoresist from a surface. The method involves contacting the surface with a composition comprising: an alkylene carbonate; optionally, either an alcohol, glycol ether, or a dibasic ester; and, optionally, water or hydrogen peroxide, and allowing the composition to contact  
30 the surface for a period of time, and under conditions effective to cause stripping of the photoresist. Optionally, the composition may be heated. Preferably, the composition is at a temperature from about 20°C to about 50°C when the surface is contacted with said composition. More preferably, the composition is at a temperature from about 25°C to about 45°C when the surface is contacted with said composition.

According to the method of the present invention, the composition may be contacted with the photoresist coated surface using any suitable method. Preferably, the composition is contacted with the photoresist coated surface by immersing the surface in the composition.

A variety of factors may influence the amount of time it takes the composition to remove the photoresist from the surface. Such factors may include temperature, photoresist type, photoresist thickness, etc. In general, the stripping times may vary from less than about 50 seconds to about 10 minutes, although longer stripping times may be observed, depending on the conditions.

The following examples are illustrative of the present invention, and are not intended to limit the scope of the invention in any way.

#### Example

The following photoresist remover composition samples were mixed in the following proportions (weight percent):

Table 1

Sample	BC <sup>1</sup>	BA <sup>2</sup>	PC <sup>3</sup>	H <sub>2</sub> O	DB <sup>4</sup>	PM <sup>5</sup>	DBE <sup>6</sup>	DGA <sup>7</sup>	FST <sup>8</sup>	IPA <sup>9</sup>
1	10			80	10					
2	10			80		10				
3				80				20		
4	50					50				
5			50			50				
6		40	9.8						50.2	
7			75							25
8	75									25
9			100							
10	100									
11			9.8				40		50.2	
12			50				50			

Sample	BC <sup>1</sup>	BA <sup>2</sup>	PC <sup>3</sup>	H <sub>2</sub> O	DB <sup>4</sup>	PM <sup>5</sup>	DBE <sup>6</sup>	DGA <sup>7</sup>	FST <sup>8</sup>	IPA <sup>9</sup>
13	50						50			
14		50	50							
15	50	50								
16			10	80	10					
17			10	80		10				
18		40	9.8						50.2	
19			9.8				40		50.2	

<sup>1</sup> Butylene carbonate, commercially available from the Huntsman Corporation, Houston, Texas under the trade name JEFFSOL® BC.

<sup>2</sup> Benzyl alcohol.

5 <sup>3</sup> Propylene carbonate, commercially available from the Huntsman Corporation, Houston, Texas under the trade name JEFFSOL® PC.

<sup>4</sup> Diethylene glycol butyl ether.

<sup>5</sup> Propylene glycol methyl ether.

<sup>6</sup> Dibasic ester ("DBE"), commercially available from DuPont.

10 <sup>7</sup> Diglycolamine® Brand of 2-(2-aminoethoxy)ethanol ("DGA®"), commercially available from the Huntsman Corporation, Houston, Texas.

<sup>8</sup> The JEFFSTRIP™ FST composition used in this Example comprised a mixture of 43% by weight of a 35% H<sub>2</sub>O<sub>2</sub> solution and 57% by weight of JEFFSOL® PC.

<sup>9</sup> Isopropyl alcohol.

15 Beakers were then filled with each of the samples mixed in Table 1, and heated to about 45°C (except samples 18 and 19). Then, two inch square wire boards that were coated with a negative photoresist were placed in each beaker. The stripping time for each sample was visually observed. Table 2 summarizes the stripping times for each sample:

Table 2

Sample	Stripping Time
1	1 minute, 50 seconds
2	6 minutes
3	<50 seconds
4	<50 seconds
5	<50 seconds

Sample	Stripping Time
6	<50 seconds
7	1 minute, 2 seconds
8	1 minute, 16 seconds
9	3 minutes, 40 seconds
10	3 minutes, 30 seconds
11	1 minute, 1 second
12	2 minutes, 10 seconds
13	2 minutes, 12 seconds
14	1 minute, 40 seconds
15	1 minute, 42 seconds
16	3 minutes, 50 seconds
17	no stripping
18	3 minutes, 40 seconds*
19	3 minutes, 43 seconds*

\* at 25°C.

Table 2 shows that the samples containing an alkylene carbonate and either: (i) propylene glycol methyl ether (samples 4 and 5) or (ii) benzyl alcohol and JEFFSTRIP™ FST (sample 6) were as effective at stripping the photoresist from the board as a conventional photoresist stripper containing DGA® (sample 3). Table 2 also shows that the samples containing an alkylene carbonate and either: (i) water and diethylene glycol butyl ether (sample 1), (ii) an alcohol (samples 7, 8, 14, and 15), or (iii) DBE and JEFFSTRIP™ FST (sample 11) showed stripping times less than two minutes. Further, samples comprising an alkylene carbonate and DBE showed stripping times less than 3 minutes (samples 12 and 13).

Further, while observing the stripping times, it was noted that the solutions without JEFFSTRIP™ FST only caused the photoresist to peel away from the metal board, while the solutions containing JEFFSTRIP™ FST actually dissolved the photoresist.

The correlation between stripping time and temperature for two photoresist samples is shown in Table 3:

Table 3

Sample	Temperature	Stripping Time
9.8% JEFFSOL®PC, 50.2% JEFFSTRIP™, and 40% benzyl alcohol	25°C	3 min., 40 sec.
	45°C	< 50 sec.
9.8% JEFFSOL®PC, 50.2% JEFFSTRIP™, and 40% DBE	25°C	3 min., 43 sec.
	45°C	1 min., 1 sec.

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Table 3 shows that increasing the temperature of the remover solution decreases the stripping time. Yet, even at the lower temperature (*i.e.* 25°C), the stripping times are well within acceptable limits.

Although illustrative embodiments have been shown and described, a wide range of  
10 modification, changes, and substitution is contemplated in the foregoing disclosure. In some instances, some features of the disclosed embodiments may be employed without a corresponding use of the other features. Accordingly, it is appropriate that the appended claims be construed broadly and in a manner consistent with the scope of the invention.



## Claims

What is claimed is:

1. A composition useful as a photoresist remover that comprises an alkylene carbonate, and optionally, either an alcohol, glycol ether, or a dibasic ester.
- 5 2. The composition of claim 1, further comprising water.
3. The composition of claim 1, further comprising hydrogen peroxide.
- 10 4. The composition of claim 1, wherein the composition contains at least about 30 percent by weight of the alkylene carbonate.
5. The composition of claim 4, wherein the composition contains at least about 20 percent by weight of an alcohol.
- 15 6. The composition of claim 4, wherein the composition contains at least about 20 percent by weight of a glycol ether.
7. The composition of claim 1, wherein the alkylene carbonate comprises propylene carbonate.
- 20 8. The composition of claim 1, wherein the alkylene carbonate comprises butylene carbonate.
- 25 9. The composition of claim 1, wherein the alcohol is selected from the group consisting of benzyl alcohol, isopropyl alcohol, methanol, and ethanol.
10. The composition of claim 1, wherein the glycol ether is selected from the group consisting of diethylene glycol butyl ether and propylene glycol methyl ether.
- 30 11. A composition useful as a photoresist remover that comprises at least about 5% by weight of an alkylene carbonate, and from about 0% to about 60% by weight of either an alcohol, a dibasic ester, or a glycol ether.
- 35 12. The composition of claim 11, further comprising water.

13. The composition of claim 11, further comprising hydrogen peroxide.
14. The composition of claim 11, wherein the alkylene carbonate comprises propylene carbonate.
15. The composition of claim 11, wherein the alkylene carbonate comprises butylene carbonate.
16. The composition of claim 11, wherein the alcohol is selected from the group consisting of benzyl alcohol, isopropyl alcohol, methanol, and ethanol.
17. The composition of claim 11, wherein the glycol ether is selected from the group consisting of diethylene glycol butyl ether and propylene glycol methyl ether.
18. A method for removing photoresist from a surface comprising the steps of:
- a. contacting the surface with an effective amount of a composition that comprises an alkylene carbonate, and optionally, either an alcohol, glycol ether, or a dibasic ester; and
  - b. allowing the composition to contact the surface for a period of time and under conditions effective to cause the removal of the photoresist from the surface.
19. The method of claim 18, wherein the composition further comprises water.
20. The method of claim 18, wherein the composition further comprises hydrogen peroxide.
21. The method of claim 18, wherein the composition contains at least about 30 percent by weight of the alkylene carbonate.
22. The method of claim 18, wherein the alkylene carbonate comprises propylene carbonate.
23. The method of claim 18, wherein the alkylene carbonate comprises butylene carbonate.

24. The method of claim 18, further comprising the step of heating the composition.
25. The method of claim 18, wherein the photoresist is a negative photoresist.
- 5 26. The method of claim 18, wherein the composition is at a temperature from about 20°C to about 50°C when the surface is contacted with the composition.
27. A method for removing photoresist from a surface comprising the step of:
- 10 a. contacting the surface with an effective amount of a composition that comprises at least about 5% by weight of an alkylene carbonate, from about 0% to about 60% by weight of either an alcohol, a dibasic ester, or a glycol ether; and
- 15 b. allowing the composition to contact the surface for a period of time and under conditions effective to cause the removal of the photoresist from the surface.
28. The method of claim 27, wherein the composition further comprises water.
29. The method of claim 27, wherein the composition further comprises hydrogen peroxide.
- 20 30. The method of claim 27, wherein the alkylene carbonate comprises propylene carbonate.
- 25 31. The method of claim 27, wherein the alkylene carbonate comprises butylene carbonate.
32. The method of claim 27, further comprising the step of heating the composition.
- 30 33. The method of claim 27, wherein the photoresist is a negative photoresist.
34. The method of claim 27, wherein the composition is at a temperature from about 20°C to about 50°C when the surface is contacted with the composition.